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DISCLAIMER

ABSTRACT

A three-year contract for the project, DOE Contract No. DE-FG26-01BC15364, "Improving CO_2 Efficiency for Recovering Oil in Heterogeneous Reservoirs," was started on September 28, 2001. This project examines three major areas in which CO_2 flooding can be improved: fluid and matrix interactions, conformance control/sweep efficiency, and reservoir simulation for improved oil recovery. The project has received a one-year, no-cost extension to September 27, 2005. During this extra time additional deliverables will be 1) the version of MASTER that has been debugged and a foam option added for CO_2 mobility control and 2) adsorption/desorption data on pure component minerals common in reservoir rock that will be used to improve predictions of chemical loss to adsorption in reservoirs.

This report discusses the activity during the six-month period covering October 1, 2003 through March 31, 2004 that comprises the first and second fiscal quarters of the project's third year. During this period of the project several areas have advanced: reservoir fluid/rock interactions and their relationships to changing injectivity, and surfactant adsorption on quarried core and pure component granules, foam stability, and high flow rate effects. Presentations and papers included: a papers covered in a previous report was presented at the fall SPE ATCE in Denver in October 2003,[1] a presentation at the Southwest ACS meeting in Oklahoma City, presentation on CO2 flood basic behavior at the Midland Annual CO2 Conference December 2003; two papers prepared for the biannual SPE/DOE Symposium on IOR, Tulsa, April 2004;[2,3] one paper accepted for the fall 2004 SPE ATCE in Houston;[4] and a paper submitted to an international journal *Journal of Colloid and Interface Science* which is being revised after peer review.[5]

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INTRODUCTION

Of the available advanced oil recovery methods, CO_2 injection has the greatest potential for improved oil recovery (IOR) from light oil reservoirs in the United States. Presently, 11 states have CO_2 injection projects, with 75% found in west Texas and southeast New Mexico. Almost universally, CO_2 injection has been a technical success when applied, and has proven profitable in the majority of reported projects. New CO_2 projects commence yearly but many reservoirs are not considered for CO_2 flooding because of low fracture pressure, poor injectivity, and/or extreme heterogeneity. The proposed work centers on crucial research to optimize CO_2 injection to maximize domestic hydrocarbon reserves. This project will expand the range of reservoirs amenable to CO_2 flooding.

During the course of our investigations, we are determining parameters and methodologies that will result in more efficient CO_2 flooding in heterogeneous reservoirs. Major areas of interests are: identifying reservoirs amenable to CO_2 flooding, characterizing CO_2 foaming agents, CO_2 flooding predictions, and parameters that effect CO_2 sweep efficiency, production rate, reservoir retention, and injectivity change effecting CO_2 and water injection rates.

Benefits will include: increasing the range of reservoirs amenable to CO_2 flooding, improving efficiency and lowering cost of CO_2 foam systems for mobility control, improving CO_2 flooding predictions, improving sweep efficiency, controlling production timing, and optimizing retention and injectivity changes.

This report discusses the activity covering October 1, 2003 through March 31, 2004 that coincides with the first and second fiscal quarter of the project's third year.

EXECUTIVE SUMMARY

A three-year contract for the project, DOE Contract No. DE-FG26-01BC15364, "Improving CO_2 Efficiency for Recovering Oil in Heterogeneous Reservoirs," was started on September 28, 2001. This project examines three major areas in which CO_2 flooding can be improved: fluid and matrix interactions, conformance control/sweep efficiency, and reservoir simulation for improved oil recovery. During this period the project received a one-year, no-cost extension to September 27, 2005. During this extra time besides completing the original task, additional deliverables will be 1) a version of MASTER that has been debugged and with a foam option added for CO_2 mobility control and 2) adsorption/desorption data on pure component minerals common in reservoir rock that will be used to improve predictions of chemical loss to satisfy reservoirs rock adsorption capacity.

This report discusses the activity during the six-month period covering October 1, 2003 through March 31, 2004 that comprises the first and second fiscal quarters of the project's third year. During this time period of the project several areas have advanced: reservoir fluid/rock interactions and their relationships to changing injectivity and surfactant adsorption on quarried core and pure component granules, foam stability, and high flow rate effects. Presentations and papers included: a paper covered in the Second Annual Report was presented at the fall SPE ATCE in Denver in October 2003,[1] a presentation at the Southwest ACS meeting in Oklahoma City, two papers prepared for the biannual SPE/DOE Symposium on IOR,[2,3] one paper accepted for the fall 2004 SPE ATCE,[4] and a paper submitted to *the Journal of Colloid and Interface Science* that is in revision after peer review.[5]

EXPERIMENTAL/RESULTS AND DISCUSSION

INJECTIVITY

The CO_2 injectivity work progresses along multiple fronts. The main coreflooding project to determine CO_2-brine-rock interaction continues. Two tests are underway and being run alternately in the same core apparatus. These systems are using tracer metals in the brine, but at much lower levels then in earlier work.[6] CO_2-brine co-injection are being performed similar to the earlier work on two types of composite cores, Indiana Salem Limestone and Ohio Lockport Dolomite. To maximize the results we are collaborating with Los Alamos National Laboratory (LANL) and University of California at Davis (UCD). PRRC runs the test, determines permeability and porosity changes periodically, and will analyze the composition of the core at the end of the test. Water samples that are taken are being analyzed by LANL for each system using tracer change to determine the dispersivity of the flooding process for scenarios of both single and double phase displacement. A high pressure sample capture device was installed into the core flood system to obtain effluent samples from the core during flooding without suffering the loss of carbonates, which normally occurs in the ambient pressure side of the effluent capture line. Imaging of the core is being done by UCD on the virgin core, at least once during the tests, and at the end of testing. This will determine how well porosity changes can be identified using imaging.

External activities include the annual CO_2 conference in Midland which included a presentation on basic CO_2-injection behavior and a visit to a Petroleum Industry Research Center to consult with project engineers and to examine well cores taken in an area that had been flooded alternately with brine and CO_2 (WAG). Figures 1 through 6 show the comparison of limestone (Figs. 1 and 2) and dolomite (Figs. 3 and 4) cores before and after being flooded in our laboratory, respectively. Field dolomite samples that had had extensive WAG flooding in the field before being cored are shown in Figs. 5 and 6. In each of the systems (Figs. 2 and 4 through 6) where CO_2 and brine have been co-injected or had had alternating injections, thus having carbonated water, show evidence of significant dissolution. The field and laboratory core have similar grainy type texture that is evidence of dissolution.

This project is seeking a better understanding of the type and scope of alterations (i.e., damage) induced in the formation by the CO_2 flooding process. For this purpose, core must be identified that reflects each state of the field (initial, water-flooded, CO_2-flooded). Primary difficulties are the general scarcity of core from the filed at he appropriate distance from a WAG injection well. The features produced by CO_2 flooding are not radically different from diagenetic processes that may occur naturally over great periods of time in nature, except in the aggressive, localized nature, and extremely high speed with which they occur during flooding. This points out the importance of locating well cores that were taken early in the life of the field to compare with laboratory flooded cores, to show the diagenetic features typical of the formation to give an indication of the scope and nature of the formation heterogeneity, and compare with changes resulting from WAG operations.

Fig. 1. Limestone before co-injection of CO_2 and brine.

Fig. 2. Limestone after co-injection of CO_2 and brine.

Fig. 3. Dolomite before co-injection of CO_2 and brine.

Fig. 4. Dolomite after co-injection of CO_2 and brine.

Fig. 5. Field dolomite core samples after WAG.

Fig. 6. Second field dolomite core sample after WAG.

SURFACTANT SCREENING

IFT and CO_2 foam stability tests continue with tests on the effects of polymers and lignosulfonates on CO_2 foam stability using the surfactant CD1045™. The polymer hydrolyzed polyacrylamide (HPAM) was prepared in 2 wt% (1.5 wt % NaCl + 0.5 wt% $CaCl_2$) brine and tested with CD1045 for the effects on IFT and foam stability. It was difficult to obtain stable IFT value for polymer solutions, as shown in the plot of concentration versus IFT in Fig. 7. This might be due to an unstable orientation of polymer at interface of CO_2 and polymer solution. The stability of CO_2-foam increased with 500 ppm HPAM in a 50 ppm solution of CD1045™ (Fig. 8). This increase was much more than both calcium (CLS) and sodium lignosulfonate (SLS), all in low concentration CD1045™ in brine. The stability was higher than expected and duplicated runs are in progress to insure that it was not caused by contamination in the lines from previous tests in the system.

SLS is being tested to determine if it is more stable in solution than CLS. However, both have been found to have precipitation and gel-like substances in solution as they age (see discussion below). The CLS solutions tend to generate more stable CO_2 foam and lower IFT than SLS solutions (see Figs. 8 and 9, respectively). As shown in earlier work,[7-9] CLS dramatically decreases the concentration of CD1045 required for stable foam. It was found that CD1045

forms weak foam with CLS at lower CD1045 concentration (50 ppm) than we had previously indicated. (Fig. 11). Weak foams might be useful in specific situations and can be used to better predict foam behavior in a reservoir situation where surfactant concentrations will vary greatly depending on dilution and adsorption effects.

In order to successfully use lignosulfonates in the field, an understanding of their stability in solutions is necessary. Precipitation and gel-like emulations have been seen in CLS and SLS solutions. Because of the organic makeup of lignosulfonates, we tested to see if this effect could be caused by bacterial growth. We found that after a mixer was seven days old and the slug was filtered, growth was limited.[5] The following tests at room temperature were performed on 5000 ppm CLS and SLS lignosulfonate solutions.

Method: Experiments were performed in the presence of light and in darkness, respectively, as follows:

1. Prepared 5000 ppm SLC and SLS solutions.
2. The control samples had no additives.
3. Boiled two samples of each and allowed to age.
4. Degassed two samples of each using ultrasonic and filled the void area with nitrogen.
5. Added 0.1 wt% formaldehyde to two samples of each.
6. Added 1 wt% sodium hypochlorite to two samples of each.
7. Added 0.1 wt% sodium azide (sodium trinitride) to two samples of each.
8. Put one of each sample type in the dark and on left in the light.

Observations:

1. Formation of gel-like flocculation in the CLS and SLS solutions were light-sensitive and the light generally increased formation of gel-like particles..
2. Adding 0.1 wt% formaldehyde or .01 wt% sodium azide prevented or minimized flocculation in both solutions.
3. Flocculation growth occurred after the sodium hypochlorite and degassing treatments.
4. Boiling caused flocculation; then, after filtration, there was little flocculation, but that might have been because many of the components reacted during boiling.

Conclusion:

These are on-going tests that may have ultimately different conclusions. At this time adding 0.1% formaldehyde to a lignosulfonate solution appears to be effective and would be a practical treatment due to operational and low cost consideration in the field application. Also formaldehyde is a common biocide used in the field. The minimum concentration required to prevent gel (bacteria) formation has not been determined.

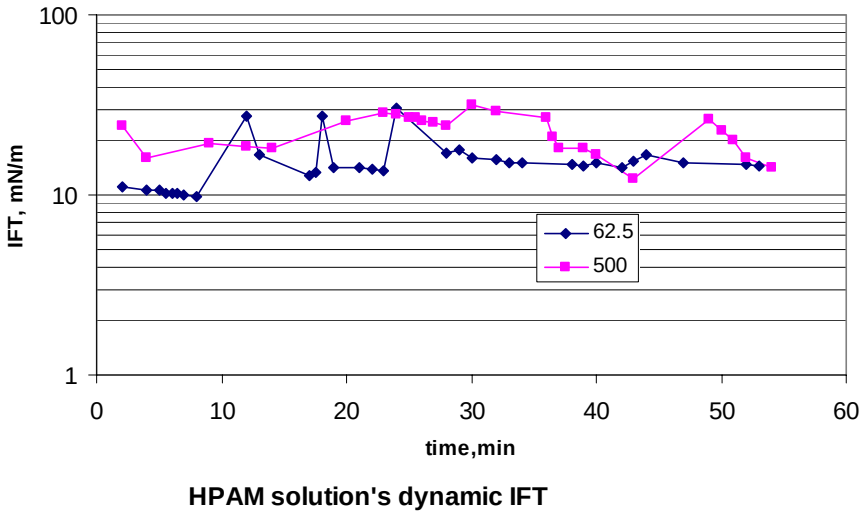
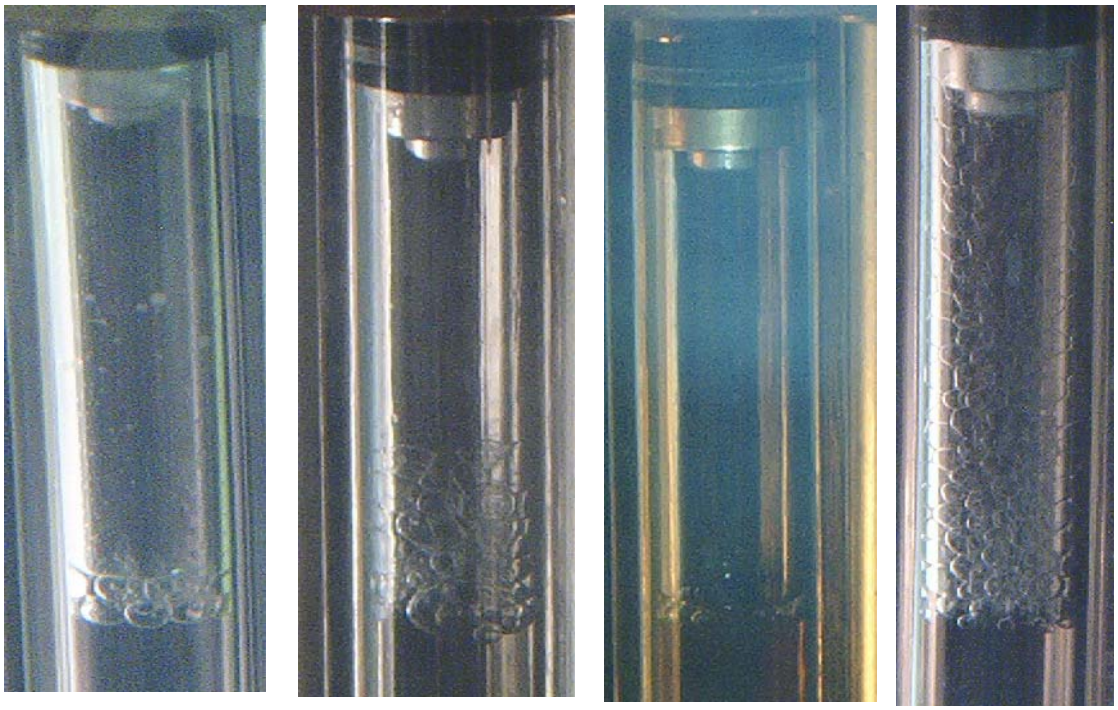


Fig. 7. IFT for HPAM at 500 and 62.5 ppm were not stable as shown in the plot. IFT appears to be slightly lower at the lower concentration, which would be unusual.



No added surfactant	0.5 wt % calcium lignosulfonate	0.5 wt% sodium lignosulfonate	0.05 wt% HPAM
----------	All with 0.005%CD1045 in 2 wt% Brine		----------

Fig. 8. Comparison of foam stability for CLS, SLS, and HPAM in a low concentration CD1045 solution.

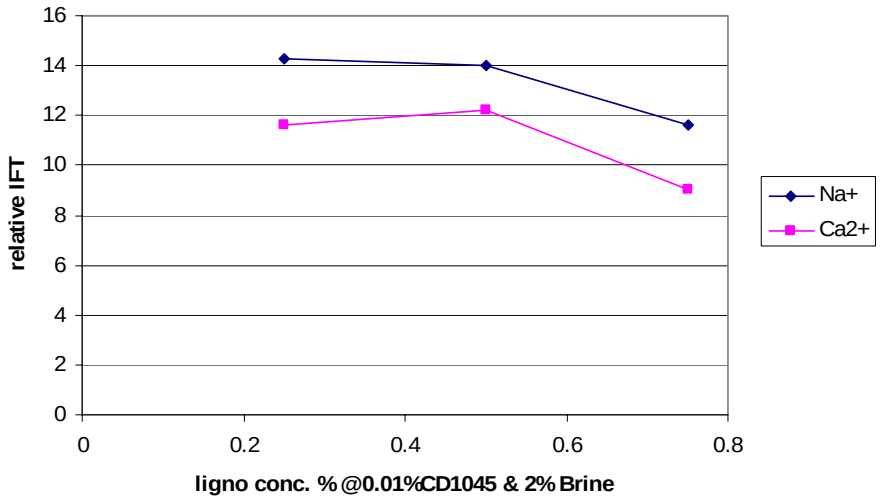


Fig. 9. IFT comparison for CLS and SLS solutions.

SORPTION TESTS

During the past six months we have looked at CD1045 adsorption and desorption onto non-porous minerals (powder) compared to porous material. Five powders of pure components often found in porous reservoir rock (montmorillonite, dolomite, kaolinite, silica and calcite) and three porous rock types were examined (Berea sandstone, limestone, and dolomite). Figure 10 shows that the equilibrium time for each of the powders was less then one hour. In each case little change in adsorption occurs after the first hour. We found that CD1045 adsorbed in decreasing order of density onto: montmorillonite, dolomite, kaolinite, silica, and calcite.

In contrast, the CD1045 adsorption onto three porous media took much longer than that onto the five non-porous media. CD1045 adsorption onto Berea sandstone required the longest time among the three porous media systems. It took about 150 hours (see Fig. 11) for adsorption to reach steady state for 500 mg/L solution of CD1045 in 2 wt% brine (1.5 NaCl and 0.5 CaCl2). It was faster for limestone and dolomite, 6 and 25 hours, respectively (Figs. 12 and 13), but still slow compared to the non-porous systems. The adsorption onto Berea appeared to have three regions possibly corresponding to three different adsorption mechanisms (Fig. 11). The curve of CD1045 adsorption onto limestone appeared to have only two regions (Fig. 12) while the dolomite might have had three, but the second region was small and could be due to acatter in the data. (Fig. 15).

Direct-flow experiments showed that desorption of CD1045 from Berea sandstone and limestone follows the exponent decline rule, similar to rate change for oil production (Figs. 14 and 15), while it is much different for dolomite (Fig.16).

With 500 ppm CD1045l, surfactant loss due to adsorption onto rock was from 34% to 84% in the three porous media (Fig. 17) with Berea having the highest adsorption. This is different from CLS, where adsorption onto limestone is higher than on Berea.

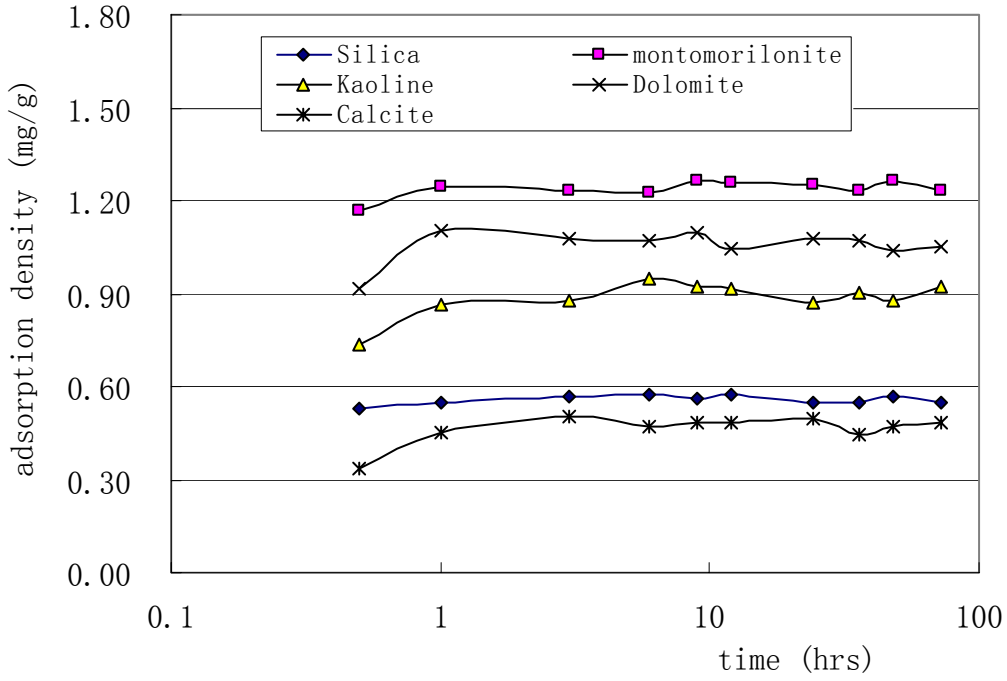


Fig.10. CD1045 adsorption versus time for five mineral powders.

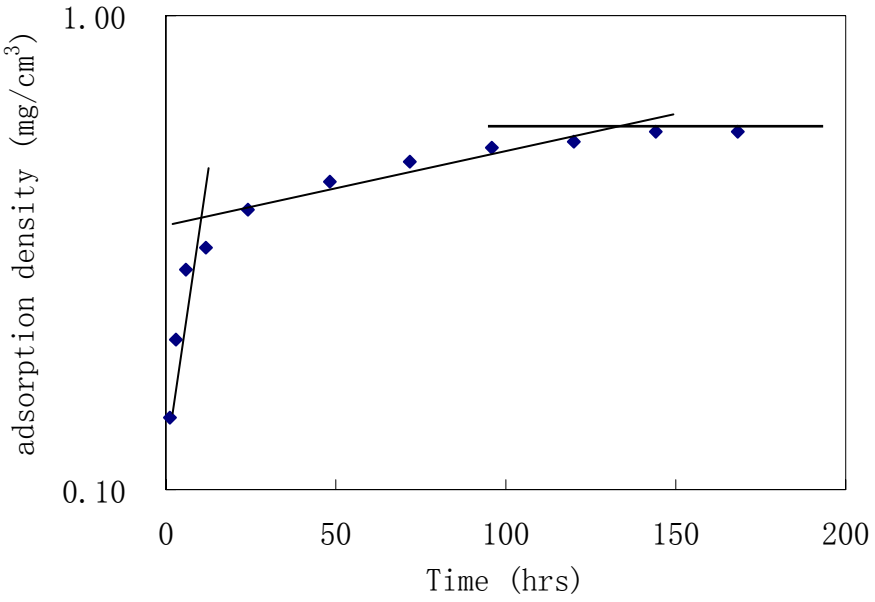
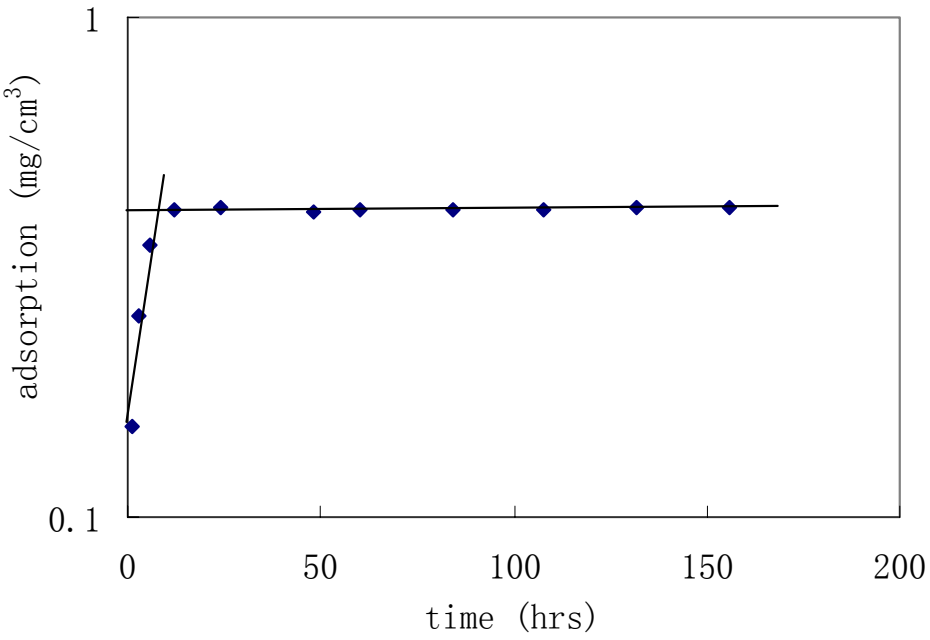


Fig. 11. A semi-log plot of CD1045 adsorption density with time (Berea).



Fig, 12.A semi-log plot of CD 1045 adsorption onto limestone.

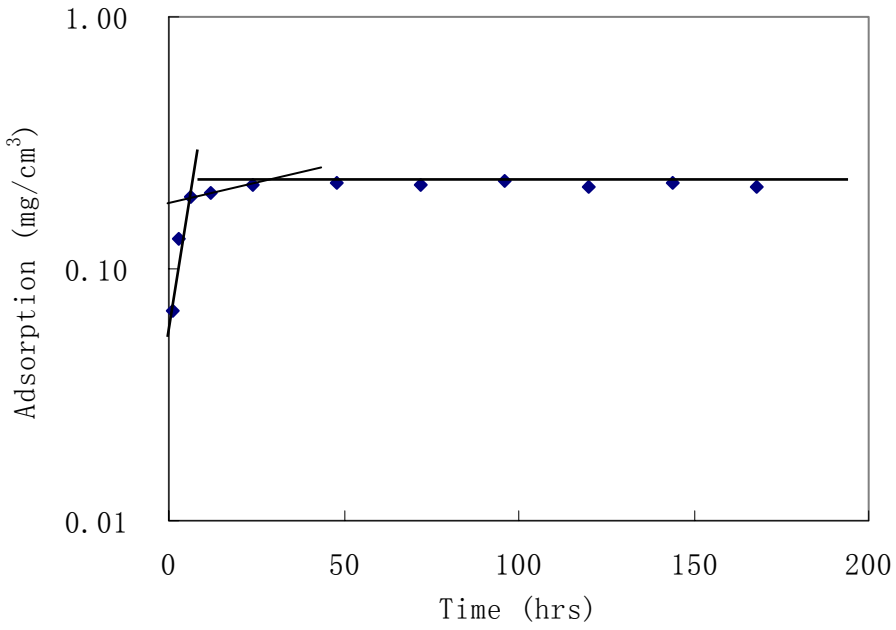


Fig. 13. A semi-log plot of CD1045 adsorption onto dolomite as a function of time.

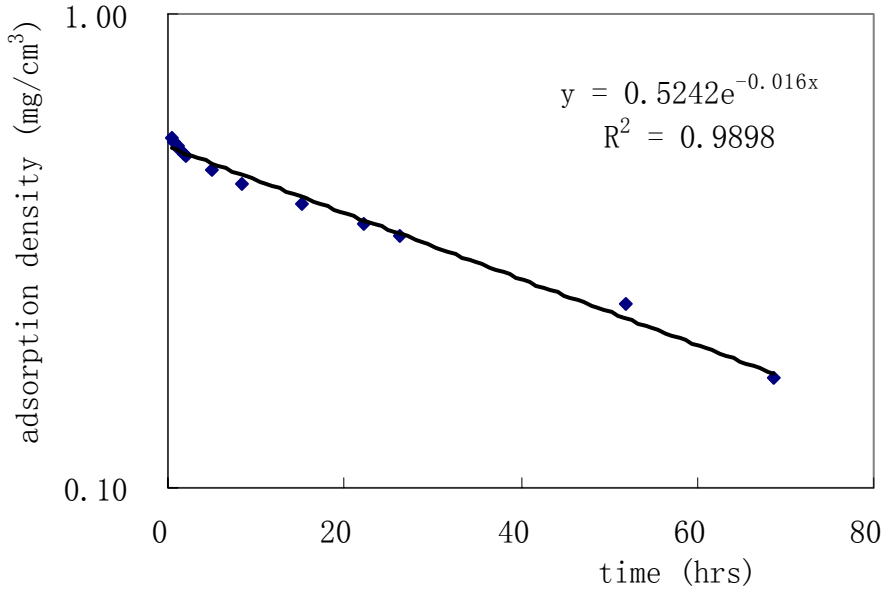


Fig. 14. CD1045 desorption from Berea sandstone as a function of time (direct flow).

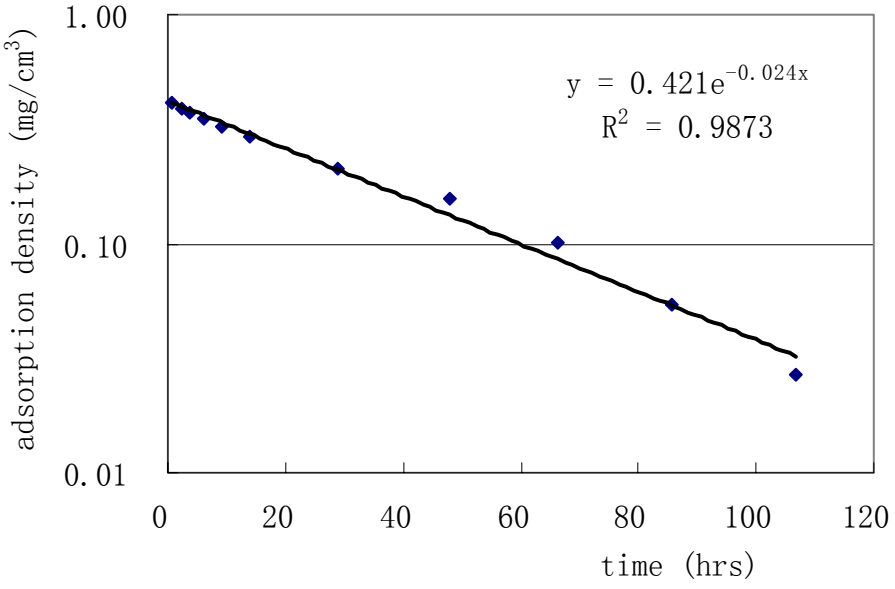


Fig. 15. CD1045 desorption from limestone as a function of time (direct flow).

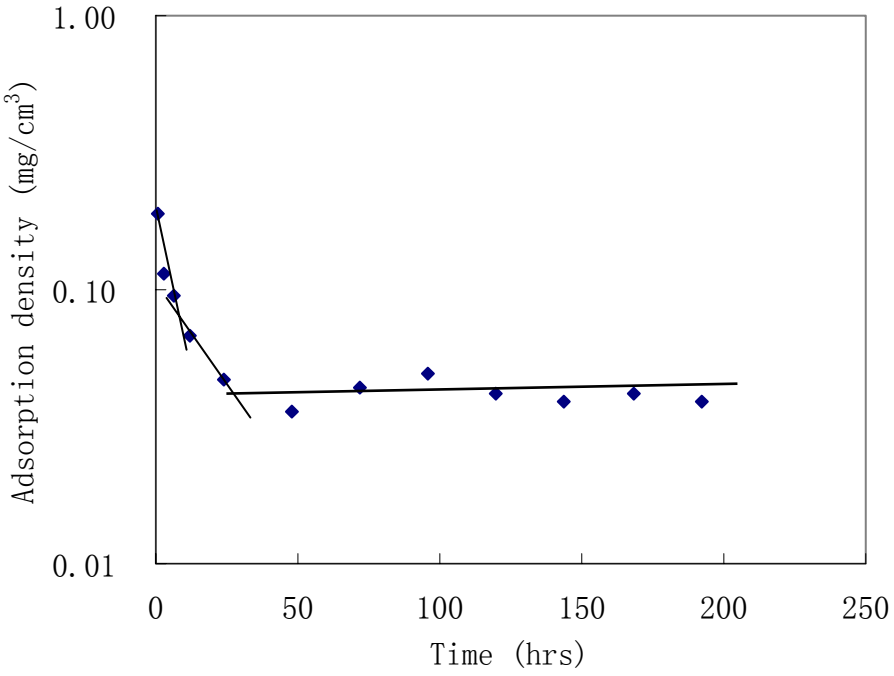


Fig. 16. Semi-log plot of CD1045 desorption from dolomite as a function of time.

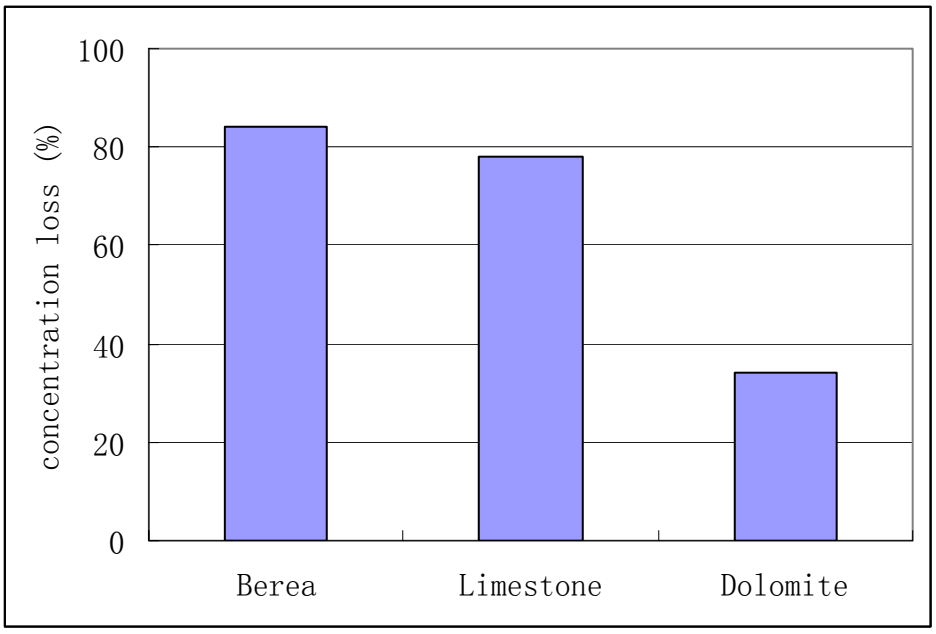


Fig. 17. Surfactant loss due to adsorption onto three porous media using 500 ppm CD1045.

MODELING AND SIMULATIONS

General sensitivity equations have been developed for non-Darcy flow parameters to effective stresses. Using these equations, the change of non-Darcy flow parameters induced by change of reservoir pressure and in-situ stresses can be calculated. The equations were based on typical reservoir conditions of pressure, temperature, porosity and permeability,[1-3] making them applicable to a wide variety of reservoir conditions. This confirmed the low (zero) sensitivities of non-Darcy parameters to shear stresses in a wider variety of reservoir conditions of pressure.

We are progressing in our efforts to model CO_2 flooding mechanisms. One of our goals is to document revisions and subroutines added to MASTER (Miscible Applied Simulation Techniques for Energy Recovery) over the past few years at New Mexico Tech's Petroleum Recovery Research Center. In the past few months, several versions of MASTER and other related tools for future development, application, and verification of changes made earlier to MASTER at the PRRC have been collected. These included: MASTER Ver. 2.0 from US DOE, developed by Ammer, J.R., Brummert, A.C. and Sams, W.N. in Feb 1991, MASTER modified by Shih-Hsien Chang in before 2000 (Incomplete), and MASTER modified by Dacun Li in 2001 (Incomplete). Also, Digital Visual Fortran Version 5.0 developed by Digital Equipment Corporation (1997) has been installed and will be used as a development tool for completing MASTER in the future.

In order to compare results from MASTER and also for work related to testing mechanisms in a commercial simulation, we have obtained and installed an industrial simulator for modeling CO_2 flooding behavior under different conditions. This is Eclipse Version 2003A_1 developed by Schlumberger and its partners. Training on using this simulator is underway. Practical application is expected in the near future.

CONCLUSIONS

1. Injectivity analyses on two core systems are running parallel using a low concentration metal tracer in the injection brine. Examination of core from a WAG-flooded reservoir confirmed structure changes noted in the laboratory.

2. IFT and stability tests comparisons were performed for calcium and sodium lignosulfonates. Also, tests to determine methods to minimize or eliminate solid or gel formation in lignosulfonates are nearing completion.
3. A laboratory test was performed to evaluate surfactant adsorption/desorption in both porous and non-porous media using five pure minerals and three porous rocks.
4. Several presentations and papers have been completed and several others have been accepted for future presentation or publication.
5. Work was completed on near-well, high-flow rate tests to determine injectivity and productivity implications.

TECHNOLOGY TRANSFER:

Paper SPE 89431: "Laboratory Investigation of Stress-Sensitivity of Non-Darcy Gas Flow Parameters," presented at the SPE/DOE 14th IOR Symposium in Tulsa, OK April 17-21, 2004.

Abstract: Non-Darcy flow parameters were investigated in 159 series of high pressure/high temperature/high velocity gas flooding experiments on five different rock samples under field reservoir conditions. The results of these experiments reconfirm and extend to new conditions that permeability increase, while non-Darcy flow coefficient decreases with effective stresses; both are independent of shear stresses. General formulas have been developed to quantify the stress-sensitivity in terms of nominal non-Darcy parameters. General equations have been proposed to predict the change of permeability and non-Darcy flow coefficient with given effective stresses and nominal non-Darcy flow parameters.

SPE 89471: "Comparison of Non-Darcy Flow of CO_2 and N_2 in a Carbonate Rock," presented at the SPE/DOE 14th IOR Symposium in Tulsa, OK April 17-21, 2004.

Abstract: This work presents the non-Darcy behavior results of CO_2 compared to the previous work using N_2. This work is based on 85 series of high-velocity gas flooding experiments under high-pressure and high-temperature. Based on experimental results, it was found that pore pressure has more influence on permeability in CO_2 flooding than that in N_2 flooding. In contrast, temperature has definite and consistent influence on both permeability and non-Darcy flow coefficient in N_2 flooding, but the same influence in CO_2 flooding was not observed. Mechanism behind these differences is attributed to physical property differences of the two gases. Much of

the work was near the CO_2 critical point or liquid regions. Other anomalies are attributed to thermal effects caused by expansion cooling of the CO_2. Field data indicates that this phenomenon could be responsible for productivity loses in high CO_2 wells. Accordingly, attention should be paid to avoid flowing CO_2 at conditions near its critical point.

"Calcium Lignosulfonate Adsorption and Desorption on Berea Sandstone," submitted to the Journal of Colloid and Interface Science.

Abstract. This paper describes adsorption and desorption studies carried out with calcium lignosulfonate (CLS) on Berea sandstone. Circulation experiments were performed to determine CLS adsorption isotherms and the effects of CLS concentration, temperature, salinity, brine hardness, and injection rate on adsorption density. Flow-through experiments were performed to assess the reversibility of CLS adsorption and the influence of postflush rate, brine concentration, brine hardness, brine pH, and temperature on the desorption process. Results indicate that CLS adsorption isotherms on Berea sandstone follow the Freundlich Isotherm law. The results presented in this paper on the effects of CLS adsorption and desorption on Berea sandstone show that: (1) increasing CLS concentration and salinity increases CLS adsorption density; (2) increasing temperature will decrease adsorption density; (3) increasing injection rate of CLS solution will slightly decrease CLS adsorption density; (4) post-flush rate and salinity of brine have a large impact on the CLS desorption process; (5) the adsorption and desorption process are not completely reversible; and (5) temperature and pH of the postflush brine have little effect on desorption.

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